

# PATENT COOPERATION TREATY

## PCT

### INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY (Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

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Applicant's or agent's file reference <b>349041P</b>	<div style="display: flex; justify-content: space-between;"> <span><b>FOR FURTHER ACTION</b></span> <span>See Form PCT/IPEA/416</span> </div>	
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Applicant <b>THE UNIVERSITY OF WESTERN ONTARIO ET AL</b>		
1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36. 2. This REPORT consists of a total of <u>5</u> sheets, including this cover sheet. 3. This report is also accompanied by ANNEXES, comprising: a. <input checked="" type="checkbox"/> (sent to the applicant and to the International Bureau) a total of <u>18</u> sheets, as follows: <input checked="" type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions). <input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. 1 and the Supplemental Box. b. <input type="checkbox"/> (sent to the International Bureau only) a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in electronic form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions). 4. This report contains indications relating to the following items: <input checked="" type="checkbox"/> Box No. I      Basis of the report <input type="checkbox"/> Box No. II     Priority <input type="checkbox"/> Box No. III    Non-establishment of opinion with regard to novelty, inventive step and industrial applicability <input type="checkbox"/> Box No. IV    Lack of unity of invention <input checked="" type="checkbox"/> Box No. V     Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement <input type="checkbox"/> Box No. VI    Certain documents cited <input checked="" type="checkbox"/> Box No. VII    Certain defects in the international application <input checked="" type="checkbox"/> Box No. VIII   Certain observations on the international application		
Date of submission of the demand 02 August 2005 (02-08-2005)	Date of completion of this report 15 February 2006 (15-02-2006)	
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# INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.  
PCT/CA2004/001773

## Box No. I Basis of the report

1. With regard to the language, this report is based on:
  - ☒ the international application in the language in which it was filed
  - ☐ a translation of the international application into \_\_\_\_\_, which is the language of a translation furnished for the purposes of:
    - ☐ international search (Rules 12.3(a) and 23.1(b))
    - ☐ publication of the international application (Rule 12.4(a))
    - ☐ international preliminary examination (Rules 55.2(a) and/or 55.3(a))
2. With regard to the elements of the international application, this report is based on (*replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report*):
  - ☐ the international application as originally filed/furnished
  - ☒ the description:
    - ☒ pages 2-6, 8-10, 13, 14, 16, 18 and 23-29 as originally filed/furnished
    - ☒ pages\* 1,7,11,12,12a,15,17,17a and 19-22 received by this Authority on 6 September 2005
    - ☐ pages\* received by this Authority on \_\_\_\_\_
  - ☒ the claims:
    - ☐ pages as originally filed/furnished
    - ☐ pages\* as amended (together with any statement) under Article 19
    - ☒ pages\* 30-35 received by this Authority on 6 September 2005
    - ☐ pages\* received by this Authority on \_\_\_\_\_
  - ☒ the drawings:
    - ☒ pages 1 - 7 as originally filed/furnished
    - ☐ pages\* received by this Authority on \_\_\_\_\_
    - ☐ pages\* received by this Authority on \_\_\_\_\_
  - ☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing.
3. ☒ The amendments have resulted in the cancellation of:
  - ☒ the description, pages pages 1, 7, 11, 12, 15, 17 and 19-22 as originally filed
  - ☒ the claims, Nos. 1 - 33 as originally filed
  - ☐ the drawings, sheets/figs
  - ☐ the sequence listing (*specify*):
  - ☐ any table(s) related to sequence listing (*specify*):
4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
  - ☐ the description, pages
  - ☐ the claims, Nos.
  - ☐ the drawings, sheets/figs
  - ☐ the sequence listing (*specify*):
  - ☐ any table(s) related to sequence listing (*specify*):

\* If item 4 applies, some or all of those sheets may be marked "superseded."

## INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.  
PCT/CA2004/001773**Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

## 1. Statement

Novelty (N)	Claims	1 to 37	YES
	Claims	none	NO
Inventive step (IS)	Claims	1 to 37	YES
	Claims	none	NO
Industrial applicability (IA)	Claims	1 to 37	YES
	Claims	none	NO

## 2. Citations and explanations (Rule 70.7)

Reference is made to the documents cited in the Written Opinion (WO) of the International Searching Authority, denoted as D1 to D5.

Novelty and Inventive Step - Articles 33(2) and 33(3) PCT

As pointed out in the WO, the claimed subject matter appears to be novel in view of documents D1 to D5. On 6 September 2005, Applicant amended the originally filed set of claims under Article 34 PCT. The amended claims have retained novelty. Thus, current claims 1 to 37 are considered to comply with Article 33(2) PCT.

With regard to the question whether the current claims involve an inventive step, documents D1 and D2 appear to be most relevant. In any case, no doubt remains that D1 combines a thermoplastic elastomer (TPE), such as an SBS or SEBS block copolymer with an *uncrosslinked soft* elastomer, particularly an EPR, as well as with a high specific gravity filler in the presence of an inert polymer. Likewise, it seems clear that D2 combines a TPE and a high specific gravity filler with a rigid thermoplastic polymer, such as PP. Thus, if a skilled person had replaced the rigid thermoplastic polymer component in a composition disclosed in D2, with the soft elastomer component of D1, he or she would probably have arrived at a composition within the scope of at least some of Applicant's claims, for example, of current claims 1 and 27.

At the same time, it is appreciated that none of documents D1 to D5 seems to teach or suggest the replacement of a *rigid* thermoplastic polymer with a *uncrosslinked soft* elastomer, such as an EPR. Even in combination, these documents do not appear to hint at such a replacement or to motivate a skilled person to carry out a replacement of this kind. Furthermore, it becomes apparent from the state of the art at the claim date that replacing a rigid thermoplastic polymer with an uncrosslinked soft elastomer is not common practice in the art and is not generally regarded as a day-by-day workshop improvement. It tends to follow that, as amended, claims 1 to 37 are believed to involve an inventive step and to comply with Article 33(3) PCT.

Industrial Applicability - Article 33(4) PCT

Claims 1 to 37 are considered to define industrially applicable subject matter and to comply with Article 33(4) PCT.

**INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY**

International application No.  
PCT/CA2004/001773

**Box No. VII      Certain defects in the international application**

The following defects in the form or contents of the international application have been noted:

On page 1 of the description, Applicant refers to an unpublished United States application. This document has not been identified adequately.

On page 12 of the description, the meaning of the last sentence remains unclear, particularly at lines 31 and 32.

**Box No. VIII** Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

Claims 1, 12 to 14, 23, 27 to 31 and 34 to 37 do not comply with Article 6 PCT for the following reasons:

- (1) In claims 1, 12 to 14 and 31, the "sufficiently high specific gravity material" and "high specific gravity material" lack an adequate definition. Furthermore, the claimed ammunition or composite material which contains this high specific gravity material without any additional boundary, does not draw sufficient support from the description. The description states at page 6, lines 4 to 6:

"This has been achieved in the present invention by using a composite material including a compacted mixture of fine metal powder, a thermoplastic block copolymer and an elastomer." (emphasis added)

In this regard, Applicant suggests in its response dated 6 September 2005 that a metal or metal oxide powder is only a preferred embodiment of the above high specific gravity material, and any sufficiently high specific gravity material may be suitably employed in the claimed ammunition or composite material. This suggestion appears to be based on a statement at page 14, lines 4 to 6 of the description, namely:

"Within the above preferred criteria, therefore any particulate high specific gravity material may be used as this component of the composite of the invention." (emphasis added)

The "above preferred criteria" inevitably refer to criteria concerning the high specific gravity material which are set forth in the preceding lines of page 14 and on pages 6 to 13 of the description. These criteria include, inter alia, the previously quoted statement from page 6 which requires the presence of a fine metal powder or, in view of further statements in the description, of a metal oxide powder. It seems to follow that a fine metal or metal oxide powder is an essential component of the ammunition or composite material defined in each of claims 1, 12 to 14 and 31. This conclusion draws further support from the fact that the description does not appear to show any evidence for the utility of any high specific gravity material other than a fine metal or metal oxide powder.

- (2) In claims 23 and 27, the value of the threshold dynamic mechanical compression creep is not defined. Whereas the term "dynamic mechanical compression creep" is, of course, well known in the art, these claims fail to show what its threshold value is. Moreover, the description appears to require a threshold creep of not higher than 20 % for the claimed ammunition or composite material. In particular, Applicant states at page 17, lines 6 and 7 of the description: "Materials with creep higher than 20 % would have poor shape retention." Since claims 23 and 27 set forth that the claimed ammunition or composite material maintains its shape, it tends to follow that the same ammunition and composite material have a threshold dynamic mechanical compression creep of 20 %.
- (3) The polymer-based ammunition of claim 28 has no antecedent in claim 27. Instead, claim 27 is directed to a composite material. Likewise, the composite materials of claims 29 to 31 have no antecedent in claim 28. Furthermore, the composite material of claim 34 lacks antecedent in claims 26 and 28 as these two claims are directed to polymer-based ammunitions. In a similar way, the polymer-based ammunitions of claims 35 and 36 lack antecedent in claims 27 and 29 to 33, and the polymer-based ammunition of claim 37 lacks antecedent in claims 27 and 29 to 34. Instead of a polymer-based ammunition, claims 27 and 29 to 34 define composite materials. It appears that Applicant might wish to direct claims 28 and 35 to 37 to a composite material rather than a polymer-based ammunition.

## LESS-LETHAL AMMUNITION PROJECTILE

### CROSS REFERENCE TO RELATED U.S. APPLICATION

5 This patent application relates to, and claims the priority benefit from,  
United States Provisional Patent Application Serial No. 60/507,491 filed on  
October 2, 2003.

### FIELD OF THE INVENTION

10 The present invention relates to polymeric-based non-lethal  
ammunition which may be used for the purpose of crowd control or by special  
task forces, e.g. SWAT teams and/or air marshals. More particularly the  
present invention relates to a composite material, which is a thermoplastic  
elastomer (TPE)-elastomer blend exhibiting shape retention. Adding a higher  
density constituent to increase the density gives a composite useful for non-  
15 lethal ammunition.

### BACKGROUND OF THE INVENTION

20 In many types of confrontational situations, the use of lethal  
ammunition is not appropriate. More and more law enforcement and military  
authorities are seeking ways to reduce casualties in confrontation situations,  
particularly crowd control and in hostage situations, which are handled by  
special task forces, e.g. SWAT teams and air marshals. Different available  
less-lethal devices have been evaluated and categorized in terms of their  
effectiveness and potential in the context of law enforcement ("Less Lethal  
25 Technologies- Initial Prioritisation and Evaluation," by T. Donnelley, Home  
Office, PSDB No 12/01, Police Scientific Development Branch, Hertfordshire,  
United Kingdom (2002)" –with permission to quote). In this report, the impact  
type of less-lethal ammunition projectiles were placed in Category A, i.e.  
those devices meriting immediate further research. Examples of less-lethal  
30 ammunition projectiles given were bean bags, sock rounds, single and  
multiple ball rounds, fin stabilized rubber projectiles, single and multiple baton  
rounds and encapsulated rounds.

Fin stabilized rubber projectiles (referred to as the Rocket) are made of  
thermoset elastomers, for example EPDM (Ethylene-Propylene-Diene

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provides added value, such as significantly less toxicity or pollutant. Since the elastomer phase is not chemically crosslinked, the composite can be recycled, but keeps its shape due to the presence of the TPE.

Accordingly, the present invention provides a polymer-based ammunition, comprising a composite material including a polymer matrix including at least one thermoplastic elastomeric polymer (TPE) component, and at least one soft elastomeric polymer component; particles of a sufficiently high specific gravity material that are dispersed in the polymer matrix and present in an amount such that the composite material has a specific gravity of in a range from about 2 to 3 grams per cubic centimeter; and the composite material having a shape of a pre-selected projectile.

The composites thus prepared are subjected to a molding process, by which cylindrical bodies from the said composite, e.g. projectiles for firearms, etc., are manufactured by standard polymer processing techniques such as injection molding.

The present invention also provides composite material, comprising: a polymer matrix including at least one thermoplastic elastomeric polymer (TPE) component, and at least one soft elastomeric polymer component, the thermoplastic elastomeric polymer (TPE) component including a block copolymer having at least one elastomeric block, the material characterized in that it exhibits a dynamic mechanical compression creep below a threshold creep so that the composite material maintains its shape.

Further features and advantages of the present invention, as well as the structure and operation of various embodiments of the present invention, are described below in detail.

### BRIEF DESCRIPTION OF DRAWINGS

The following is a description, by way of example only, of the new projectile, material properties of the composites constructed in accordance with the present invention, where IIR = butyl elastomer (isobutylene isoprene rubber); SIBS = polystyrene-*block*-polyisobutylene-*block*-polystyrene, reference being had to the accompanying drawings, in which:

maximum allowable deflection of 6.93 mm and the maximum tolerable impact force without serious injury is limited to 3200 N. With the desirable 76 ms<sup>-1</sup> (250 fts<sup>-1</sup>) muzzle velocity, this translates into about 15 g and 25 g mass for the 20 and 12-gauge projectiles, respectively. Thus the minimum density of the projectiles with the dimensions shown in Figure (1) was calculated to be 2.4 gm-cm<sup>-3</sup>.

The next criterion was the selection of materials that would yield the desired mechanical properties. Butyl elastomer (IIR) has outstanding low temperature properties and very high damping, but has very high creep without crosslinking (J. V. Fusco and P. House, in "Rubber Technology," M. Morton, Ed., Van Nostrand Reinhold Company, New York (1987). The inventors contemplated that a blend of novel polyisobutylene-based styrene-isobutylene-styrene SIBS TPE (J. P. Kennedy, J. E. Puskas, G. Kaszas, and W. G. Hager (to the University of Akron, U.S. Patent 4,946,899, Aug. 7, 1990, and J.E.Puskas, C. Paulo, P. Antony, to UWO, US Patent 6,747,098, 2004), and butyl elastomer, filled to achieve the required minimum density of 2.4 g/cm<sup>-3</sup>, would be a promising composite for less-lethal ammunition. TPEs, including SIBS, show processing behavior similar to that of thermoplastics and mechanical properties similar to that of thermoset elastomers or rubbers. Therefore they combine the advantages of low fabrication cost and recyclability with elasticity and softness (G. Holden and N. R. Legge, in "Thermoplastic Elastomers-A Comprehensive Review," G. Holden, N. R. Legge, R. Quirk, H. E. Schroeder (Eds.), Hanser Publishers, Munich (1996)).

Styrenic block-type thermoplastics elastomers (SBS and SIS) have been commercialized since the 1960s and are available in a wide range of hardness, depending on the rubber/plastic ratio. SIBS have been developed in the last decade and only recently have been commercialized. Preliminary testing demonstrated that SIBS with its inherent high damping properties due to the polyisobutylene segment would eminently be suitable for developing a composite for the novel less-lethal projectiles. Moreover, the exceptional low temperature properties of these block copolymers together with ease of processing and recyclability, make them suitable candidates for low temperature application. The SIBS would provide a "physically crosslinked network", thereby ensuring shape retention combined with recyclability. With



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the advent of macromolecular engineering, scientists gained control over polymerization processes and are able to produce various polymer architectures, shown in Figure 1a.

5 Linear triblock SIBS TPEs are considered the first generation of these new materials and were introduced commercially in 2003 by Kaneka Co. of Japan, based on a license of U.S. No. Patent 4,946,899, from the University of Akron. Star-branched SIBS is considered the second generation, with improved properties, and has not been commercialized yet. The third generation, arborescent (dendritic, tree-like) SIBS TPEs are disclosed in U.S.  
10 Patent No. 6,747,098, 2004 issued to Puskas et al. Initial investigations of the mechanical and viscoelastic properties of these materials indicated superior properties (P. Antony, Y.Kwon, J.E. Puskas, M. Kovar, P.R. Norton, EUR. POLYM. J., 40, 149-157, (2003) and Y. Kwon, J. E. Puskas, A.Bhowmick, J. POLYM. SCI., CHEM., 43, 1811 (2005)). All of these SIBS-type TPEs can  
15 serve as "physical crosslinking agents" of the butyl (IIR) elastomer matrix of the current invention. Any type of commercial butyl elastomer can be used as the elastomeric component of the composite in the present invention.

In order to achieve the desired density of the composite, an appropriate filler is required. As stated earlier, the use of lead in the less-lethal market is  
20 not favourable, due to its environmental toxicity.

The present invention, and preferred embodiments of the various aspects thereof, will now be described in detail. The essence of the present invention lies in a special bi-component polymer matrix that provides the composite with desirable balance of physical properties, notably softness and  
25 compression creep and high damping property combination with required high density.

The polymer matrix of the composite of this invention comprises at least one soft elastomeric polymer component and at least one thermoplastic elastomeric polymer component. These composite materials have utility in  
30 applications requiring shape retention, and particularly, when combined with a filler as described above is very useful in producing polymer-based ammunition.

Suitable polymers for use in the invention as the soft elastomeric polymer component include polyisobutylene, polyisobutylene-isoprene copolymers, polyisobutylene-styrene copolymers, polyisobutylene- alkyl styrene copolymers, halogenated polyisobutylene- alkyl styrene terpolymers,

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generally important that the content of the softer, elastomeric component is not too high or too low compared with the content of the harder thermoplastic elastomeric polymer component.

The polymer matrix of the composite of the invention preferably comprises the soft elastomeric polymer component in an amount within the range from about 25 to about 90% by weight of the polymer matrix, more preferably from about 40 to about 60% by weight, and the thermoplastic elastomeric polymer component in an amount within the range from about 10 to about 75% by weight, more preferably from about 60 to about 40% by weight.

Preferably the high density composite of the invention has a hardness value, as measured according to the Shore A scale, in the range of from about 30 to about 55. A hardness of less than about 30 Shore A gives a product which is generally too soft for applications such as shot or bullets for firearms, where the projectile would tend have compression creep higher than 20% which makes them unsuitable as they have higher probability of getting stuck in the barrel.

The composite of the present invention may be manufactured by conventional methods well known in polymer technology, as are well known to the person skilled in the art and well described in the literature. For example, the rigid thermoplastic elastomeric polymer and soft elastomeric polymer components are heated to above their glass transition temperature and one of these components is added to the other with mixing in a standard type of mixer until the TPEs are not completely homogeneous even in the molten state optionally with further heating if necessary. Once the matrix is fully mixed and while the mixture is still in its molten or at least soft state, the high specific gravity particulate material is added, with further mixing in order to evenly disperse the particles in the matrix. Mixing may be continued until complete dispersion is achieved, following which the composite may be cooled and passed to the next processing stage, which is preferably the formation of discrete bodies of the composite by molding, for example injection molding or compression molding.

Compression creep data provides information on the ability of the material to maintain its shape. High creep means high permanent deformation. A thermoset (crosslinked) rubber typically has about 5 % creep, corresponding to excellent ability to maintain the shape of the article. A typical thermoplastic elastomer has somewhat higher creep (10-15%), still associated with good shape retention. Materials with creep higher than 20% would have poor shape retention. (J. V. Fusco and P. House, in "Rubber Technology," M. Morton, Ed., Van Nostrand Reinhold Company, New York (1987)). Thus, polymer-based ammunition can be produced having a dynamic mechanical compression creep below a threshold creep so that the polymer-based ammunition maintains its shape for a pre-selected period of time. The threshold creep is preferably about 20%. By selection of the compositions of the different constituents, materials can be produced to retain their shape for a pre-selected period of time, for example a preferred composition can be produced which does not change more than 10% for at least a year.

### Example 3

Example 2 is repeated, with the following modifications. Iron powder (Atomet 67), butyl elastomer (grade RB301) and polyisobutylene-polystyrene block co-polymer (Kaneka grade SIBS073T) in weight ratios (iron:elastomer : block co-polymer, 70 : 22.5 : 7.5) were mixed into a composite material. The Shore A hardness of this composite, hereafter referred as SIBS25, determined according to ASTM standard D2240, was 23 and the density was 2.42 gcm<sup>-3</sup>. The compression creep of SIBS25 determined by DEFO, at a load of 75 Newton and 40°C was 22% (Figure 2).

### Example 4

Example 2 is repeated, with the following modifications. Iron powder (Atomet 67), butyl elastomer (grade RB301) and polyisobutylene-polystyrene block co-polymer (Kaneka grade SIBS073T) in weight ratios (iron:elastomer : block co-polymer, 70 : 15 : 15) were mixed into a composite material. The

Shore A hardness of the composite, hereafter referred as SIBS50, determined according to ASTM standard D2240, was 36 and its density was 2.44 g/cm<sup>3</sup>. The dynamic mechanical compression creep of SIBS50 determined by DEFO, at a load of 75 Newton and 40°C was 12% (Figure 2).

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#### Example 5

Example 2 is repeated, with the following modifications. Iron powder (Atomet 67), butyl elastomer (grade RB301) and polyisobutylene-polystyrene block copolymer (Kaneka grade SIBS073T) in weight ratios (iron: elastomer:

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gradually increased with frequency for all composites (Figure 3). The plots of SIBS50 and SIBS75 run close and somewhat above the plot of IIR, but both of them are considerably lower than the SIBS composite in the whole frequency range, with the difference increasing at higher frequencies. At higher frequencies, there is no considerable flow of polymer chains within the short period of oscillation and the material behaves like a glassy solid, hence an increase in  $E'$  with frequency is observed. All the elastomeric composites showed more or less same tan delta (Figure 4) at higher frequencies, but the IIR composite showed higher tan delta at lower frequencies. The tan delta increase of the composites at high frequency could be due to partial breakdown in the physical cross-links.

In the previous Example 3 it has been shown that incorporation of SIBS polymer to the composite is essential for the shape retention of the less lethal ammunition. In addition to this incorporation of SIBS thermoplastic elastomer also increases the modulus of the composite. If the bullet made from polymer-metal has modulus higher than the desired value, it would be hard and would impart higher energy to the target and can become lethal. Whereas, if the modulus of the composite is less than desired, the less lethal projectile made out of it would become ineffective. With addition of SIBS thermoplastic elastomer the shape retention property and the modulus of the polymer-metal composite can be simultaneously optimized as per requirement and the polymer-metal composite can be used for making a less lethal ammunition.

### Example 8

Dynamic Mechanical Analysis was carried out at  $0^{\circ}\text{C}$  (Figures 5 and 6).  $E'$  slightly increased below 1 Hz, followed by a rapid increase and leveling off at about 100 Hz (Figure 5). At  $0^{\circ}\text{C}$  and higher frequencies, there is no flow of polymer chains within the short period of oscillation hence the modulus increases with frequency. All the elastomeric composites had more or less same tan delta (Figure 6), which gradually increased in the higher frequency range (1 - 500 Hz). This again could be due to the partial breakdown in the physical cross-links.

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**Example 9**

Dynamic Mechanical Analysis was carried out at -50 °C (Figures 7 and 8). The storage modulus plot of the SIBS50 composite was very close to the plot of IIR, with SIBS75 and SIBS100 showing higher moduli in the entire range (Figure 7). The tan delta plots of all composites run close to each other (Figure 8), decreasing up till about 10 Hz and levelling off in the higher frequency range.

In summary, these results show that IIR and SIBS25 have low Shore A Hardness (Table I), but display high compression creep behavior. SIBS75 had almost the same compression creep as SIBS50 composite but had higher Shore A Hardness and moduli. SIBS100 had lower compression creep and higher Shore A Hardness than the other composite mixes. Based on this analysis the SIBS50 (IIR/SIB/Iron 50/50/233) seems to have optimum hardness, compression creep and dynamic mechanical properties for less-lethal ammunition projectile application.

**Example 10**

Comparative dynamic mechanical analysis between different existing less lethal ammunition and the newly developed less lethal ammunition was carried out with the MTS instrument, at a dynamic load of 1% strain in a frequency range of 0.15 to 500 Hz at 50 °C and 0 °C (Figures 9-12). At 50 °C, SIBS50 showed lower modulus compared to rocket, tube and mono-ball projectiles (Figure 9). The tan delta of SIBS50 was lower than that of the rocket projectile and the tube projectile but slightly higher than the mono-ball projectile up to about a 100 Hz, beyond which both of the mono-ball and SIBS50 showed increasing but similar tan delta values (Figure 10). At 0 °C, the E' plot of SIBS50 runs below the plots of the rocket projectile and the tube projectile, and close to that of the mono-ball projectile until about 10 Hz (Figure 11). In the higher frequency range (10- 500 Hz), the modulus of SIBS50 showed a sharp increase, reaching the values of the rocket projectile. The tan delta (Figure 12) of the new less-lethal ammunition projectile was somewhat lower than the rocket and tube projectiles, but higher than the mono-ball, up to about 10 Hz, when it started to increase, surpassing the

existing projectiles. This indicates very good low temperature properties in the high frequency range.

At -50 °C, it was not possible to perform dynamic mechanical analysis for rocket and tube projectiles since their modulus exceeded the force limit of the load cell of the instrument. The dynamic mechanical analysis in the temperature range of 50 – 0 °C, indicates that at higher frequencies the new projectile has lower modulus, indicating lower hardness and higher tan delta, with better damping properties than the existing rocket and tube projectiles.

### Example 11

Less-lethal projectiles produced in accordance with the present invention were fired at a velocity of about 250 ft/s (~ 75 m/s), thus the estimated frequency range of 12% deformation upon impact is about 16,000 to 21,000 Hz (~102,000 to 132,000 rad/s). Stiffness analysis in a wide frequency range (dynamic stiffness) with the application of the Time-Temperature Superposition (TTS) principle, a method well known in the art of polymer rheology, was used to compare the performance of various less lethal projectiles. Figure 13 shows the plots, with the firing frequency range marked. Above 102 rad/sec, the SIBS50 showed much lower stiffness than the commercial less lethal ammunition – within the estimated firing frequency range the difference is 2-3 orders of magnitude. Therefore, the new SIBS/IIR composite is expected to have superior performance compared to existing less lethal ammunition.

### Example 12

#### New method for comparative impact testing

The composite SIBS50 offers the most advantages in terms of compression creep properties (11% DEFO) and hardness (36 Shore A). A comparative impact testing of the new less lethal ammunition projectile developed using SIBS50 (described in Example 4) was carried out using a novel DOW Styrofoam Impactor. The Impactor arrangement consists of polystyrene foam sheets (commercially named Styrofoam SM made by DOW. It is a viscoelastic material allowing for penetration of rubber projectiles. Four 2'x 2'x 2"-sheets are placed upright and strapped tightly to insure a proper



hold. The stack of sheets is then placed against a fixed surface such as a brick wall to prevent tumbling. Current tests show that at 15-foot firing distance from the muzzle and  $300 \pm 15$  ft/sec muzzle velocity (measured using a Doppler Radar) results in a penetration of about 6 inches in the foam.

Impact Energy transfer is then calculated as a function of the projectile's penetration in the foam by the following equation:

$$\text{Impact Energy (J)} = A \times L_p \times \text{Compressive Strength (0.21 MPa)}$$

Where:

A= projectile's impact cross sectional area.

$L_p$ = length of projectile penetration in the foam.

The accuracy and the impact energy of less-lethal projectile made of SIBS50 were compared with sock rounds for 12-gauge and 20-gauge projectiles; Tables 2-5 summarize the results. The sock round was selected for this comparative test since it is the most widely used less lethal projectile in market and has proven to be the best of all existing less lethal projectiles, despite of being associated with some serious injuries to human targets. The calculated impact energies were compared with the impact energy corridors proposed by Bir. The clay impactor set-up used by Bir requires significant conditioning at a very narrow temperature and humidity range, thus its use is rather cumbersome. We tested the projectiles using the novel Styrofoam impactor introduced here. Styrofoam is an insulating hydrophobic viscoelastic material that maintains constant mechanical properties over a broader range of temperatures and humidity.

Tables 2 and 3 summarize test results for the 20-gauge less-lethal projectiles. The projectile distance from center of target was  $9.30 \pm 2.00$  cm with an average velocity of  $84 \pm 5.27$  ms<sup>-1</sup> for the new projectile, and  $7.24 \pm 3.28$  cm with an average velocity of  $91.91 \pm 7.17$  ms<sup>-1</sup> for the sock round. One of the main factors in judging the performance of less-lethal projectiles is its velocity consistency. A velocity deviation less than 10% is regarded excellent when using less-lethal projectiles. The velocity deviation for the newly developed 20-gauge projectile was about 6.3%, in comparison with about 7.8% for the sock round. The second main factor is the impact area of the projectile. Both the newly developed 20-gauge projectiles and the sock

**THEREFORE WHAT IS CLAIMED IS:**

1. A polymer-based ammunition, comprising:  
a composite material including  
a polymer matrix including at least one thermoplastic elastomeric polymer (TPE) component, and at least one soft elastomeric polymer component;  
particles of a sufficiently high specific gravity material that are dispersed in the polymer matrix and present in an amount such that the composite material has a specific gravity of in a range from about 2 to 3 grams per cubic centimeter; and  
the composite material having a shape of a pre-selected projectile.
2. The polymer-based ammunition according to claim 1 wherein the thermoplastic elastomeric polymer (TPE) component comprises a block copolymer having at least one elastomeric block.
3. The polymer-based ammunition according to claim 2 wherein the thermoplastic elastomeric polymer (TPE) component is selected from the group consisting of polystyrene-polyisobutylene block copolymers, polystyrene-polybutadiene block copolymers, polystyrene-polyisoprene block copolymers, polystyrene-poly(ethylene-butylene block copolymers, polystyrene-poly(ethylene-propylene) block copolymers, thermoplastic polyolefins (TPOs), and dynamically vulcanized TPVs.
4. The polymer-based ammunition according to claim 1, 2 or 3 wherein the thermoplastic elastomeric polymer (TPE) component has a structure selected from the group consisting of linear, star, arborescent, comb, brush, centipede, hyperbranched, and dendritic.
5. The polymer-based ammunition according to claim 1, 2, 3 or 4 wherein the elastomeric polymer component is selected from the group consisting of

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polyisobutylene, polyisobutylene-isoprene copolymers, polyisobutylene-styrene copolymers, polyisobutylene- alkyl styrene copolymers, halogenated polyisobutylene- alkyl styrene terpolymers, polybutadiene, polyisoprene, polyethylene-propylene copolymers, polyethylene-propylene diene terpolymers.

6. The polymer-based ammunition according to claim 1, 2, 3 or 4 wherein the elastomeric polymer component is polyisobutylene, and wherein the thermoplastic elastomeric polymer (TPE) component is polystyrene-polyisobutylene-polystyrene (SIBS).

7. The polymer-based ammunition according to claim 1, 2, 3 or 4 wherein the elastomeric polymer component is a polyisobutylene-isoprene copolymer, and wherein the thermoplastic elastomeric polymer (TPE) component is polystyrene-polyisobutylene-polystyrene (SIBS).

8. The polymer-based ammunition according to claim 1, 2, 3, 4, 5, 6 or 7 wherein the elastomeric polymer component is present in an amount from about 10% to about 90% by weight of the polymer matrix, and wherein the thermoplastic elastomeric polymer component is present in an amount from about 90 to about 10% by weight of the polymer matrix.

9. The polymer-based ammunition according to claim 1, 2, 3, 4, 5, 6 or 7 wherein the elastomeric polymer component is present in an amount from about 40% to about 60% by weight of the polymer matrix, and wherein the thermoplastic elastomeric polymer component is present in an amount from about 60 to about 40% by weight of the polymer matrix.

10. The polymer-based ammunition according to claim 5 wherein the elastomeric polymer component has a structure selected from the group consisting of linear, star, arborescent, comb, brush, centipede, hyperbranched and dendritic.

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11. The polymer-based ammunition according to claim 1, 2, 3, 4 or 5 wherein the specific gravity of the composite material is at least about 2.44 grams per cubic centimeter.
12. The polymer-based ammunition according to claim 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 or 11 wherein the high specific gravity material is present in the composite material in an amount of from about 50 to about 90% by volume of the total composite.
13. The polymer-based ammunition according to claim 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 or 11 wherein the high specific gravity material is present in the composite material in an amount of from about 60 to about 80% by volume of the total composite.
14. The polymer-based ammunition according to claim 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 or 11 wherein the high specific gravity material is present in the composite material in an amount of from about 10 to about 90% by volume of the total composite.
15. The polymer-based ammunition according to any one of claims 1 to 4 wherein the composite material has a cylindrical or spherical shape.
16. The polymer-based ammunition according to any one of claims 1 to 15 having a hardness value, as measured according to the Shore A scale, in a range of from about 15 to about 80.
17. The polymer-based ammunition according to any one of claims 1 to 15 having a hardness value, as measured according to the Shore A scale, in a range of from about 30 to about 55.
18. The polymer-based ammunition according to any one of claims 1 to 17 wherein the particles of a high specific gravity material are selected from the group consisting of iron powder, tungsten, copper, bismuth, and iron oxide.

19. The polymer-based ammunition according to any one of claims 1 to 17 wherein the particles of a high specific gravity material are iron powder particles.
20. The polymer-based ammunition according to claim 19 wherein the iron powder particles have sizes in a range from about 71.4% of -100 to +325 U.S. Mesh and 23.2% of -325 U.S. Mesh, specific gravity, 7.8 gcm<sup>-3</sup>.
21. The polymer-based ammunition according to any one of claims 1 to 20 produced by molding the composite material into any one of a cylindrical or spherical shape.
22. The polymer-based ammunition according to claim 21 wherein the step of molding is one of injection molding and compression molding.
23. The polymer-based ammunition according to any one of claims 1 to 22 wherein the composite material has a dynamic mechanical compression creep below a threshold creep so that the polymer-based ammunition maintains its shape.
24. The polymer-based ammunition according to any one of claim 23 wherein said threshold dynamic mechanical compression creep is about 20%.
25. The polymer-based ammunition according to claim 23 wherein dimensions of the composite material do not change more than 10% for at least a year.
26. The polymer-based ammunition according to any one of claims 1 to 23 wherein the composite material has a dynamic mechanical compression creep between 4 and 20% creep.
27. A composite material, comprising:  
a polymer matrix including at least one thermoplastic elastomeric polymer (TPE) component, and at least one soft elastomeric polymer

component, the thermoplastic elastomeric polymer (TPE) component including a block copolymer having at least one elastomeric block, the material characterized in that it exhibits a dynamic mechanical compression creep below a threshold creep so that the composite material maintains its shape.

28. The polymer-based ammunition according to claim 27 wherein the thermoplastic elastomeric polymer (TPE) component is selected from the group consisting of polystyrene-polyisobutylene block copolymers, polystyrene-polybutadiene block copolymers, polystyrene-polyisoprene block copolymers, polystyrene-poly(ethylene-butylene block copolymers, polystyrene-poly(ethylene-propylene) block copolymers, thermoplastic polyolefins (TPOs), and dynamically vulcanized TPVs.

29. The composite material according to claim 27 or 28 wherein the elastomeric polymer component is selected from the group consisting of polyisobutylene, polyisobutylene-isoprene copolymers, polyisobutylene-styrene copolymers, polyisobutylene- alkyl styrene copolymers, halogenated polyisobutylene- alkyl styrene terpolymers, polybutadiene, polyisoprene, polyethylene-propylene copolymers, polyethylene-propylene diene terpolymers.

30. The composite material according to claim 27, 28 or 29 wherein the thermoplastic elastomeric polymer (TPE) component and the elastomeric polymer component have a structure selected from the group consisting of linear, star, arborescent, comb, brush, centipede, hyperbranched, and dendritic.

31. The composite material according to claim 27, 28, 29 or 30 including particles of a high specific gravity material that are dispersed in the polymer matrix and present in an amount such that the composite material has a specific gravity of in a range from about 2 to 3 grams per cubic centimeter.

32. The composite material according to claim 31 wherein the particles of a high specific gravity material are selected from the group consisting of iron powder, tungsten, copper, bismuth, and iron oxide.

33. The composite material according to claim 31 wherein the particles of a high specific gravity material are iron powder particles.

34. The composite material according to claim 26, 27, 28, 29, 30, 31, 32 or 33 wherein the elastomeric polymer component is one of polyisobutylene and polyisobutylene-isoprene copolymer.

35. The polymer-based ammunition according to any one of claims 26 to 33 wherein said threshold dynamic mechanical compression creep is about 20%.

36. The polymer-based ammunition according to any one of claims 26 to 35 wherein the composite material has a dynamic mechanical compression creep between 4% and 20% creep.

37. The polymer-based ammunition according to any one of claims 27 to 34 wherein dimensions of the composite material do not change more than 10% for at least a year.